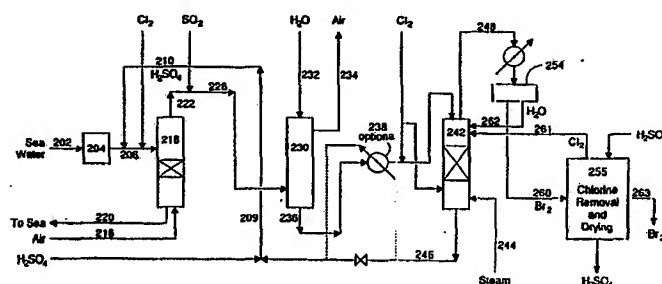




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(54) Title: PROCESS FOR PRODUCING BROMINE FROM SEAWATER**(57) Abstract**

This invention is a combination process for producing elemental bromine using a seawater feed. The process involves a series of steps in which seawater is acidified, chlorinated, and air stripped to remove the bromine. The stripping effluent is reacted with an SO_2 stream to convert the bromine to hydrogen bromide and H_2SO_4 in the air stream. The process continues by absorbing hydrogen bromide and H_2SO_4 from the resulting acidic fog to produce an aqueous H_2SO_4 stream containing HBr . The HBr is stripped from the liquid stream and passed to an oxidation reactor where it is catalytically oxidized with an oxygen-containing gas to produce a stream of Br_2 and H_2O . The hot reactor effluent is quenched and the product Br_2 is separated from the H_2O and inert gases such as air. In the figure 2 seawater enters pipeline (202) and is mixed with an H_2SO_4 stream (200). The resulting stream (214) is sent to a stripping column (218) where air stream (216) strips the bromine from the liquid. The vapor B22 stream (222) is mixed with SO_2 (224) which is contacted with a water stream. The resulting aqueous $\text{H}_2\text{SO}_4/\text{HBr}$ stream (236) is heated and mixed with a chlorine stream (240). A portion of the chlorine is introduced through line (241) to the bottom of stripping column (242) and separates with stream (244) into stream (246) containing H_2O_4 and HCl separates with stream (244) into stream (246) containing H_2SO_4 and HCl and stream (248) containing Br_2 . The Br_2 product (260) is discharged from decanter (254) into the purification unit (255).

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5 PROCESS FOR PRODUCING BROMINE FROM SEAWATERField of the Invention

 This invention is a combination process for
producing elemental bromine using a seawater feed. The
10 process involves a series of steps in which seawater is
acidified, chlorinated, and air stripped to remove the
bromine. The stripping effluent is reacted with an SO_2
stream to convert the bromine to hydrogen bromide and
 H_2SO_4 in the air stream. The process continues by
15 absorbing hydrogen bromide and H_2SO_4 from the resulting
acidic fog to produce an aqueous H_2SO_4 stream containing
HBr. The HBr is stripped from the liquid stream and
passed to a oxidation reactor where it is catalytically
oxidized with an oxygen-containing gas to produce a
20 stream of Br_2 and H_2O . The hot reactor effluent is
quenched and the product Br_2 is separated from the H_2O and
any inert gases such as air,

Background of the Invention

25 This invention is a process for producing
elemental bromine from hydrogen bromide recovered from
seawater involving a catalytic oxidation step. The
catalytic oxidation step permits the inventive process to
eliminate nearly 50% of the chlorine requirements of the
30 known processes.

 Bromine is a chemical feedstock often used for
the production of bromoalkanes or olefins from alkanes.
Bromine is present in nature only in dilute sources such
as in seawater or in brines of the Dead Sea or the United
35 States. The classic process for producing bromine from

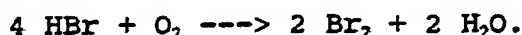
seawater involves a multistage process of acidifying and chlorinating the brine to release elemental bromine into a solution; aerating the resulting dilute solution; reacting the bromine with SO₂ to produce hydrogen bromide and sulfuric acid; absorbing the hydrogen bromide and sulfuric acid from the aeration effluent into water; heating, chlorinating, and steaming the resulting absorbate; stripping the bromine overhead; and decanting the resulting overhead product to recover the bromine.

10 This invention includes a catalytic process sequence which may be inserted into the classic process as a substitute for the steps of heating, chlorinating, and steaming the aeration effluent. The process steps may include:

- 15 (a) stripping the aeration effluent to produce an HBr/H₂O stream,
- (b) catalytically oxidizing the HBr/H₂O stream to produce a wet Br₂ stream, and
- (c) separating the Br₂ from the water.

20 We know of no process in which elemental bromine is produced from seawater and which uses a catalyst to produce the desired Br₂.

There are a number of processes described in the open literature which produce bromine according to the equation:



One such process (British Patent 930,341) involves the conversion of hydrobromic acid solutions using dissolved metal ion catalysts. The soluble metal may be gold, cerium, chromium, nickel, platinum, thorium, titanium, or vanadium; but preferably is iron or copper. A gas containing oxygen is passed through the acidic solution containing HBr and the dissolved metal, all at a temperature below the boiling point of the liquid. The

30

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gaseous effluent is then separated via condensation and distillation into product bromine, water, and HBr for recycle to the oxidation step.

Similarly, U.S. Pat. No. 3,179,498, to Harding et al, disclose a process in which a nitrite catalyst is employed in the acidic, aqueous solution of HBr to effect the oxidation of the HBr to Br₂. The temperature of the liquid is maintained between 0° and 100°C. Although any inorganic or organic nitrite is said to be suitable, preferred catalysts are alkali or alkaline earth metal nitrites.

There are a number of processes which use heterogeneous catalysts to effect that conversion.

U.S. Pat. No. 2,536,457, to Mugdan, teaches such a process. The conversion is carried out at a temperature between 800° and 1200°C (preferably between 800° and 1000°C) with an excess of oxygen. The catalyst is preferably cerium oxide and may be supported on pumice granules or other refractory materials. If excessive water is included in the reactor, a combustible gas such as hydrogen is included to maintain the reaction temperature. Clearly the reaction temperature for this process is quite high.

U.S. Pat. No. 3,273,964, to De Rosset, shows a process in which the effluent from a dehydrobromination reaction is contacted with a catalyst-adsorbent composite. The effluent contains olefinic hydrocarbons and is produced by a series of steps in which an alkane is brominated to form a bromoalkane; the bromoalkane is then dehydrobrominated to form the effluent of olefinic hydrocarbons and HBr. The catalyst-adsorbent composite adsorbs the HBr in a first step and, during regeneration, catalyzes the oxidation of HBr to form the desired Br₂. The composite contains an adsorbent of a basic metal oxide such as magnesium, calcium, or zinc oxide, and a

catalyst of a Group IV-B metal oxide such as titania, magnesia, or zirconia. The preferred composite contains magnesia and zirconia in a ratio from about 0.5:1 to about 5:1.

- 5 U.S. Pat. No. 3,260,568, to Bloch et al, teaches a process in which a stream containing substantially dry HBr contacts a solid adsorbent containing a metal "subchloride" and which is the reaction product of a refractory metal oxide and a metal
- 10 chloride. The contact takes place at conditions where the HBr replaces at least a portion of the chloride in the adsorbent. When the adsorbent has reached about six percent by weight, the adsorbent is regenerated by contacting it with a dry hydrogen chloride gas. The
- 15 patent does not appear to suggest the conversion of the adsorbed HBr to Br₂, even though the adsorbent is suggested to be selected from metal chlorides such as aluminum, antimony, beryllium, iron, gallium, tin, titanium, and zinc chlorides.
- 20 U.S. Pat. No. 3,310,380, to Lester, discloses a process for the adsorption of combined bromine (e.g., HBr and alkyl bromides) on a catalytic-adsorbent composite, recovering unsaturated hydrocarbons, and when the adsorbent is filled, contacting the composite with an
- 25 oxygen-containing gas at a temperature between 50° and 450°C to produce a Br₂ stream also containing water and unreacted HBr. This stream (also in admixture with an oxygen-containing gas) is then contacted with a second stage reactor also containing the composite but at a
- 30 temperature between 200° and 600°C. The composite in the first stage comprises, preferably, 0.5 to 10% by weight of copper or cerium oxide composited on magnesium oxide: the second stage composite comprises, preferably, 2.0 to about 50% by weight of copper or cerium oxide composited
- 35 on an alumina or zirconia support.

Similarly, U.S. Pat. No. 3,346,340, to Louvar et al, suggests a process for the oxidation of HBr to Br₂ using a catalyst-inert support composite. The composite comprises a copper or cerium oxide on an inert support
5 having a surface area between 5 and 100 square meters per gram and containing less than about 50 micromoles of hydroxyl per gram. The supports may be alpha- or theta-alumina or zirconia. The preferred temperature is between 300° and 600°C.

10 U.S. Pat. No. 3,353,916, to Lester, discloses a two stage process for oxidizing HBr to form Br₂ by the steps of mixing the HBr-containing gas with an oxygen-containing gas and passing the mixture at a temperature of at least 225°C over a catalyst selected from the
15 oxides and salts of cerium, manganese, chromium, iron, nickel, and cobalt and converting a major portion of the HBr to Br₂. The partially converted gas, still containing excess oxygen, is then passed through a second stage catalyst comprising a copper oxide or salt at a
20 temperature of at least about 225°C but not exceeding a "catalyst peak temperature" of 350°C to convert the remaining HBr. The preferred support appears to be zirconia.

This two-stage arrangement is carried out to
25 prevent loss of copper catalyst. Because the preferred copper oxide is converted to copper bromide during the course of the reaction, at reaction conditions, and copper bromide volatilizes at "temperatures in excess of about 350°C", the "copper bromide migrates through the
30 catalyst mass in the direction of flow with eventual loss of copper bromide and premature deactivation." Use of a first catalyst stage which is tolerant of high temperatures, even though the first stage catalyst is apparently not as active a catalyst as is copper, allows
35 a cooler second catalyst stage containing copper to

complete "quantitative conversion of bromine from hydrogen bromide."

U.S. Pat. No. 3,379,506, to Massonne et al, discloses a process for the selective oxidation of hydrogen bromide to bromine in the presence of fluorocarbons by passing the mixture of gases over a Deacon catalyst at a temperature of 250 to 475°C, preferably between 300 and 400°C. The Deacon catalyst is said to be a "mostly porous carrier such as pumice, alumina, silica gel, clay, or bentonite, impregnated with a solution of bromides or chlorides of metals such as copper, iron, titanium, vanadium, chromium, manganese, cobalt, molybdenum, tungsten, or mixtures thereof." The preferred catalyst is said to be a chloride of copper. The patent notes that

"[a] very efficient and stable catalyst is an oxidation catalyst which is prepared by impregnating active alumina with chlorides of copper, rare earths and/or alkali metals, drying at about 120°C and subsequent activation at a temperature of 300° to 450°C."

One example shows the production and use of a catalyst of alumina, potassium, copper, and an amount of "rare earths of the cerite group as chlorides".

Another patent which notes the problem with the volatilization of copper bromide in the oxidation of hydrogen bromide to bromine is U.S. Pat. No. 3,437,445, to Hay et al. The solution is to eliminate the copper in favor of a noble metal, such as platinum and palladium. The reaction is carried out at a temperature of about 175° and about 700°C with a contact time of at least about 0.1 sec, "but for best operation a contact time of about five and 25 seconds is preferred." The yield of bromine is only between 28 and 78 molar percentage.

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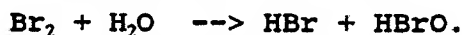
U.S. Pat. No. 4,131,626, to Sharma et al, suggests a process in which bromide salts are heated in the presence of an oxygen-containing gas, silicon dioxide, and an oxidation catalyst at a temperature of about 500° to 1000°C. The bromine is produced in conjunction with sodium silicate.

None of these documents suggest a process in which Br₂ is produced from seawater using a catalytic HBr oxidation step.

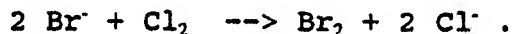
Summary of the Invention

This invention is a process for producing Br₂ from seawater in which an intermediate catalytic step comprises oxidizing hydrogen bromide with O₂ to form that elemental bromine.

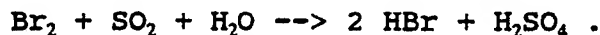
In this process, seawater is screened of solid material such as seaweed and fish and acidified with H₂SO₄ to produce an acidified stream having a pH between 3.0 and 3.5. This improves bromine recovery by suppressing the hydrolysis of bromine as it is formed:



The bromide ion in the seawater is then oxidized using chlorine:



The bromine is then stripped from the acidified, chlorinated seawater in a air stripper. The dilute bromine fog is reacted with sulfur dioxide and forms an acid fog:



This acid fog is then condensed or absorbed and introduced to a refluxed stripping column using, e.g., steam, to form a wet vaporous stream of HBr and a liquid stream of H₂SO₄. The H₂SO₄ may be recycled to the initial acidification step. The vaporous HBr is mixed with an oxygen-containing gas and heated to a temperature

between about 125°C and about 500°C. The heated gas mixture is passed over the catalyst at conditions suitable for the formation of bromine. The bromine is then separated from the feed and co-produced water by quenching, absorbing the Br₂ in a bromide salt solution and desorbing pure Br₂. The Br₂ may be further dried, if so desired.

Brief Description of the Drawings

Figure 1 shows a block diagram of a generic embodiment of the inventive process.

Figure 2 is a schematic diagram of a known process for producing Br₂ from seawater.

Figure 3 shows a schematic of a front end of a process modified from the process shown in Figure 2 providing a feedstream for the processes shown in Figures 4 and 5.

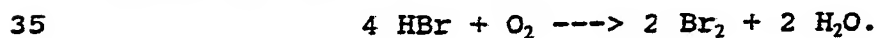
Figures 4 and 5 show preferred process embodiments of this invention as terminal portions of the Figure 3 process steps.

Figure 6 is a graph of the performance of a preferred HBr oxidation catalyst over a range of operating temperatures.

Figure 7 is a graph of the performance of a preferred HBr oxidation catalyst over a period of time.

Description of the Invention

As noted above, this invention is an improved process for producing bromine from seawater. Several of the steps of the process are from an older process in wide use. The improvement largely involves an intermediate catalytic step of oxidizing hydrogen bromide with an oxygen-containing gas to form elemental bromine according to the equation:

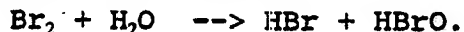


This step permits elimination of the chlorine oxidation step utilized in the older process.

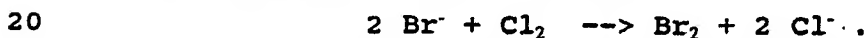
Process

5 This invention is a process for producing Br_2 from seawater in which an intermediate catalytic step comprises oxidizing hydrogen bromide to that elemental bromine. The catalyst desirably comprises a supported copper or cerium bromide but may comprise a homogeneous
10 catalyst system generally as described below.

As is shown in Figure 1, in this process, seawater is screened of solid material such as seaweed and fish and is mixed with H_2SO_4 to produce an acidified stream having a pH between 3.0 and 3.5. This improves
15 bromine recovery by suppressing the hydrolysis of bromine as it is formed in a later step:



The bromide ion in the seawater is then oxidized in the following step using chlorine:



The bromine is then stripped from the acidified, chlorinated seawater in an aerator or air stripper to form a dilute Br_2 fog and a bromine-depleted seawater stream. The dilute bromine fog is reacted with sulfur
25 dioxide and forms an acid fog:



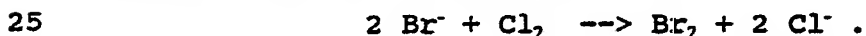
This acid fog is then condensed or absorbed using a water or weak HBr stream. The absorbed acids are then introduced to a refluxed stripping column using, e.g.,
30 steam, to form a wet vaporous stream of HBr and a liquid stream of aqueous H_2SO_4 . The H_2SO_4 may be recycled to the initial acidification step. The vaporous HBr is mixed with an oxygen-containing gas and heated to a temperature between 125°C and about 500°C . The heated gas mixture is
35 passed over the catalyst at conditions suitable for the

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formation of bromine. The reactor effluent is then quenched and the bromine separated from the feed and co-produced water. The Br₂ may be further dried, if so desired.

5 Figure 2 shows a widely used variation of a process for producing Br₂ from seawater. The bromine content of seawater varies throughout the oceans of the world but often is in the range of about 50 to 70 ppm. The bromine typically is completely ionized or nominally
10 in the form of a salt such as NaBr.

 The process involves introducing the seawater through a pipeline (202) into a solids separator (204) such as a screen or filter to remove large or entrained solids, e.g., seaweed, fish, mud and sand. The filtered
15 seawater is then transported via line (206) and thoroughly mixed with a H₂SO₄ stream (210) in that line (206). The pH level of the liquid in line (206) is maintained at about 3.0-3.5 so to prevent hydrolysis of produced Br₂. The form of mixing line (206) is obviously
20 not critical but need only be substantially resistant to corrosion at the noted conditions. The acidified seawater is then mixed with a chlorine stream (212). The bromide ion in the seawater is oxidized using that chlorine in the following manner:



 The resulting stream (214) is then sent to a packed stripping column (218) where a stream of air (216) is utilized to strip the bromine from the liquid. The resulting water stream (220) is then properly disposed
30 of, typically by returning it to the sea. The vapor stream (222) from aerator (218) is a very dilute stream of Br₂ and water usually in the form of a saturated vapor or "fog" in air. This vapor stream (222) is then mixed with sulfur dioxide (224) and forms a dilute acidic
35 vapor stream (226) of hydrobromic and sulfuric acids:

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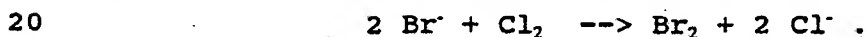
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This acid stream (226) is contacted with a water stream (232) in absorber (230). The air stream (234) is relatively clean; it may be recycled if so desired. The
5 resulting aqueous $\text{H}_2\text{SO}_4/\text{HBr}$ stream (236) is then of sufficient strength to be efficiently oxidized.

The preceding steps are common both to the well known process and to our improved process. Our
improvements are to the latter stages of the process
10 scheme and will be described in more detail below. However, to allow a proper perspective, we will describe the remainder of this widely recognized process as is shown in Figure 2.

The aqueous $\text{H}_2\text{SO}_4/\text{HBr}$ stream (236) is optionally
15 heated in exchanger (238) by feed/effluent exchange with the heated effluent stream (246) and mixed with a second chlorine stream (240) again to oxidize the bromine ion; a portion of the chlorine is introduced through line (241) to the bottom of stripping column (242):



The bromine is then stripped in a steam stripper (242). The steam (244) in steam stripper (242) separates the incoming stream into a liquid sulfuric acid/hydrochloric acid stream (246) and a gaseous Br_2 stream (248)
25 containing some Cl_2 and H_2O vapor. The gaseous $\text{Br}_2/\text{Cl}_2/\text{H}_2\text{O}$ is condensed in exchanger (249). A water phase (containing some Br_2) (262) from decanter (254) is used as reflux in column (242).

The Br_2 product (260) is discharged from the
30 bottom of the decanter (254) through line (260) into the purification unit (255). The purification unit (255) is used to remove chlorine for recycle via line (261) and drying of the Br_2 product. The Br_2 product is discharged from the unit in line (263). After drying and chlorine
35 removal, the Br_2 product stream (263) is suitable for use

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in that it contains only about 0.5-1.0 % water, but is often subjected to a drying step by contact with a strong (93-97 %) sulfuric acid stream.

In contrast to the process described just above, our process eliminates the necessity of introducing additional chlorine at (240) and (241) to oxidize the bromide ion to Br_2 and instead utilizes an oxidation step using O_2 or air to produce the Br_2 product. In practical terms, nearly half of the chlorine requirement of the prior art process is eliminated by use of our process.

Figure 3 shows a front end portion of our inventive process adapting several stages of the prior art process mentioned above and suitable for producing an HBr stream which may be used in our catalytic oxidation stage as described below with respect to Figures 4 and 5.

In the process shown in Figure 3, the solids separator (204), mixing line (206), stripping column or aerator (218), and absorber (230) are all used as in the process shown in Figure 2. In our inventive process, however, the aqueous $\text{H}_2\text{SO}_4/\text{HBr}$ stream (236) is subjected to a steam stripping step in stripper (302). In addition to the steam (304), the stripper utilizes a small reflux to prevent sulfuric acid entrainment in the overhead HBr/ H_2O (308) stream. The bottom stream (310) is typically aqueous sulfuric acid and may be used to acidify the seawater in the front end of the process. The overhead HBr/ H_2O (308) stream may be subjected to an SO_2 removal step (312) using an appropriate adsorbent or a combination of a condenser to condense the HBr/ H_2O stream, an oxidation step of converting the SO_2 to H_2SO_4 by reaction with introduced Br_2 , and a reboiled stripper column to strip HBr from the resulting liquid stream. This step may be desirable only if there is a trace of SO_2 remaining in the feedsteam. The resulting HBr stream

(314) may then be applied to the oxidation stages shown below.

Figures 4 and 5 show desirable integrated processes for the oxidation of HBr to Br₂ using the catalyst described above. Figure 4 shows a process using reasonably pure O₂ as the process feed; Figure 5 shows a process in which air is the process feed.

The oxidation step involves the simple expedient of mixing the gaseous or vaporous HBr from the feed preparation step with a suitable amount of an oxygen-containing gas, such as air, oxygen-enhanced air, or oxygen and passing the mixture to the catalyst. The O₂ is desirably added in an amount producing an HBr:O₂ molar ratio of between about 3.00 and 4.25. The O₂ may be present in excess not only to assist in the HBr oxidation but also to oxidize any hydrocarbonaceous materials present in the feedstream. Nevertheless an HBr:O₂ molar ratio of between above 3.9 and up to 4.1 is preferred.

In any event, the HBr-O₂ mixture is then passed through one or more beds of the catalysts described above. As noted elsewhere, this reaction is highly exothermic. The temperature in the reactor may be controlled in a variety of ways. For instance, if an adiabatic reactor is desired, the feed HBr likely will need be diluted with steam, nitrogen, air, product stream recycle, or the like to prevent excessive temperature rise in the reactor. Specifically, the HBr feedstream may have an HBr content of between 25% and 99.5% (wt) but desirably has an HBr content between 35% and 55% (wt) but most preferably between 45% and 55% (wt). Use of anhydrous (or highly concentrated) HBr and pure O₂ as the oxidant is difficult in that the temperature rise in an adiabatic reactor is nearly 2000°C; even the use of air and anhydrous HBr results in an adiabatic temperature

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rise of 1000°C -- a possible but unlikely candidate for ease of operation. Consequently, the use of air and an HBr feed of between 45% and 55% (wt) is very desirable and readily operable.

5 In other reactor configurations, some provision may be made for removing or controlling the heat of reaction, e.g., by inclusion of the bed or beds in an appropriately cooled heat exchanger (such as by tubes of catalyst in a steam generator), by adding the oxygen-
10 containing gas in a series of steps with cooling steps amongst sequential catalyst beds, etc. The catalyst bed or beds may be fluidized or ebullated if so desired. Fluidization allows superior control of the bed temperature and prevents the occurrence of "hot-spots"
15 in the catalyst.

 The materials of construction for the reactor should be selected using normal materials criteria but bearing in mind that the system is fairly corrosive. For instance, if the reactor is operated at the lower end of
20 the reaction range noted above and the reactor is a nickel alloy, the reactor should be maintained above the temperature of condensation lest liquid phase corrosion occur. Similarly, the upper range of temperature should be controlled to prevent vapor phase corrosion. If a
25 ceramic system is chosen, similar criteria are applicable to prevent dissolution of the ceramic or to prevent creep of the polymeric seals used at joints and flanges.

Oxygen Process

30 In the embodiment of the inventive oxidation process shown in Figure 4, an HBr stream (314) is introduced from the front end process shown in Figure 3. The HBr feedstream (preferably of about 48% HBr in water) is sent to an evaporator (404) and to a superheater
35 (406). The resulting HBr vapor should be at a

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temperature of about 230-250°C. The oxygen feedstream (408) is similarly warmed to about 230-250°C with superheater (410). The heat for superheaters (406) and (410) may, for instance, be supplied by a circulating
5 hot oil system including hot oil heater (412).

The heated HBr feedstream and the heated oxygen feedstream are then mixed to form a reactor feedstream (414) which is then introduced into reactor (416). The reactor (416) is desirably of a multi-tube design
10 containing the catalyst or may be of a multi-bed design. Since the reaction is quite exothermic, reactor designs which are capable of removing the heat of reaction from the catalyst mass are obviously very desirable. The reactor design shown is also used as a steam generator.

15 The reaction product stream (418) may then be cooled in two stages. The first stage of cooling (420) shown is a desuperheater and merely lowers the temperature of the stream down to the neighborhood of the stream's dew point, e.g., about 150°C. This stream is
20 then condensed and cooled to a temperature of about 40°C in condenser (422).

The condensate is then separated into a liquid Br₂ stream (424) saturated with water, a water stream (426) saturated with Br₂, and a vaporous vent stream
25 (428) containing unreacted oxygen, bromine, water, and a small amount of inerts. The device used for that separation (430) may be a simple phase separation device such as a decanter. Other density separation devices are just as suitable.

30 The vapor stream (428) is then chilled in refrigeration unit (432) to a temperature sufficient to remove most of the Br₂ found in the vent stream. The condensed Br₂ stream is separated in drum (432) and the resulting Br₂ stream (434) is mixed with Br₂ stream (424)
35 for further processing. The resulting non-condensed

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oxygen vapor stream (436) is scrubbed in a gas treater (438) using, for instance, sodium hydroxide remove any remaining Br_2 before the treated oxygen is vented (440) into the atmosphere. The vent gas treatment step may be omitted and recycled into the reactor (416) if the oxygen is of sufficient purity.

The aqueous stream (426) coming from the separator (432) is then stripped of its Br_2 content in a distillation column (442). Distillation column (442) produces two streams. The overhead vapor stream (444) is condensed in overhead condenser (446) and collected in reflux drum (448). The reflux drum (448) is a decanter design. The lighter phase is largely water and is recycled to the distillation tower (442) as reflux. The heavier phase is Br_2 and the stream (450) is mixed with other Br_2 streams, (424) and (434), for further treatment such as by drying with strong H_2SO_4 in a countercurrent absorption tower (456). The tower produces a weaker H_2SO_4 stream and the desired Br_2 product stream (458).

The bottom stream (452) from distillation tower (442) is partially reboiled in reboiler (454). The remainder of the stream is mostly water containing unconverted HBr feed and the water of reaction formed in the reactor (416). All or a portion of this stream may be treated by neutralization with, e.g., caustic soda, to produce a waste water stream (462). If the inventive process is used as an integrated portion of a process which is capable of using a dilute HBr , the dilute HBr stream may be so recycled.

There are other ways of eliminating the water produced in the reactor. For instance, by operating separator (432) at different conditions, e.g., at a temperature above 40°C , the overhead stream (436) will contain the water of reaction.

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Air Process

The oxidation process step is preferably operated using a less concentrated oxygen feedstream, e.g., air or oxygen-enriched air. This variation is shown in Figure 5.

In a general sense, the process scheme is similar to that used in the oxygen process stage described above. The reactor and condensation sections are identical.

As above, an HBr feedstream (314) is sent to an evaporator (504) and to a superheater (506). The air feedstream (508) is compressed in compressor (509) and heated in superheater (510). The heat for superheaters (506) and (510) may, for instance, be supplied by a circulating hot oil system including hot oil heater (512).

The heated HBr feedstream and the heated oxygen feedstream are then mixed to form a reactor feedstream (514) which is then introduced into reactor (516). The reactor (516) is desirably of a design similar to that described above although because of the additional diluent in the feedstream is a little less sensitive to reactor design, but those which are capable of removing the heat of reaction from the catalyst mass are obviously very desirable.

The reaction product stream (518) may then be cooled in two stages. The first stage of cooling (520) shown is a desuperheater and lowers the temperature of the stream down to the neighborhood of the stream's dew point, e.g., about 150°C. This stream is then condensed and cooled to a temperature of about 40°C in condenser (522). The condensed reactor product stream (524) is fed to a phase separator (526) where it is separated into an aqueous stream (528) saturated in Br₂ and containing

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any unconverted HBr and an overhead vapor stream (530) containing all of the Br_2 .

The aqueous stream (528) may be treated in a manner similar to that discussed above. The aqueous stream (528) coming from the separator (526) is stripped of its Br_2 content in a distillation column (530). Distillation column (530) produces an overhead vapor stream (532) which is condensed in overhead condenser (534) and collected in reflux drum (536). Water from the drum is recycled to the distillation tower (530) as reflux. The Br_2 stream (538) is mixed with other Br_2 streams for further treatment such as drying.

The bottom stream (540) from distillation tower (530) is reboiled. The stream is mostly water and contains unconverted HBr feed and the water of reaction formed in the reactor (516). All or a portion of this stream (542) may be neutralized to produce a waste water stream (546) or maybe recycled via line (548).

Returning to the phase separator (526), the overhead vapor stream (N_2 , Br_2 , and H_2O) may be introduced into the bottom of an absorption column (550) where cold (-15°C) lean NaBr brine (552) is fed to the top to act as absorption media for Br_2 . The overhead stream (554) is substantially free of Br_2 .

The bottom stream (556) is heated (preferably in feed-effluent heat exchanger (558) with the heat from the bottom of stripper column (560)) and introduced into stripper column (560). In that column, Br_2 is stripped from the NaBr brine into an overhead stream (562). That steam is condensed in exchanger (564) and collected in reflux vessel (566). The water stream is decanted in reflux vessel (566) and is both used as reflux in stripper tower (560) and in the feed to distillation tower (530).

The vapor line (568) from the reflux drum (566) may be mixed with the overhead vapor stream (554) from absorber (550) and treated by neutralization in absorber (570) to remove any remaining HBr before disposing of the
5 N₂ via vent (572).

The decanted Br₂ (574) from reflux vessel (566) may be mixed with the Br₂ stream (538) from reflux vessel (536) and treated with concentrated H₂SO₄ in absorber (576) to remove water and produce the dry product Br₂.
10

The Catalyst

Catalysts suitable for this process include a wide variety of supported or homogeneous materials. For instance, the active catalyst may be selected from the
15 metals; and the oxides, halides (particularly chlorides and bromides), and oxyhalides of the following metals: Group IB (particularly Cu), Group IVB (particularly Ti and Zr), Group VB (particularly V), Group VIB (particularly Cr, Mo, and W), Group VIIB (particularly Mn and Re), Group VIII (particularly Fe, Co, Ni, Pt, and
20 Pd), and the rare earth lanthanide series (particularly Ce). The active catalyst may be promoted with one or more Group IIA metals (particularly Ca) or lanthanides, if so desired. The active catalyst and the promoter, if
25 any, may be supported on known catalyst supports such as MgO, Al₂O₃ (particularly in eta- or delta-form), ZrO₂, HfO₂, SiO₂ (particularly in silica gel form), clays such as bentonite or attapulgite, and natural materials such as pumice.

30 The active catalysts listed above should be present in at least a catalytic amount, that is to say, an amount sufficient at least to catalyze the reaction of HBr and oxygen to produce Br₂. Active catalytic metals, depending upon the metal selected, may be present in the
35 amount of 0.1 % to 35 % (by weight) of the overall

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composition is desirable; 1.0 % to 20 % (by weight) of catalytic metal is more desirable and 3.0 % to 10.0 % (by weight) of catalytic metal is most desirable.

The promoters/stabilizers may be any salt or complex of the noted metals, whether oil or water soluble, which can be impregnated onto the catalyst support or mixed with the support, e.g., as by ball milling with the support precursor. The bromide salts are especially suitable, but other halides (iodide or chloride), oxyhalides, oxides, phosphates, sulfides, sulfates; complexes such as acetylacetonates, and the like are also suitable. The bromides, oxybromides, oxides, and mixtures are useful and conveniently available. The promoter/stabilizer metal-bearing material should be present in an amount such that the overall content (in whatever form) is desirably between 0.1 % and 10 % (by weight) of the overall composition; 1.0 % to 6.0 % (by weight) is more desirable; 1.0 % to 4.0 % (by weight) is most desirable.

If the catalyst support is zirconium-containing, it desirably contains more than about 50% (wt) of zirconia. A minor amount of other metal oxides, e.g., alumina, titania, yttria, silica, hafnia, etc., may be included as a binder or extrusion aid or to increase surface area if so desired. Whether the support is zirconium-containing or not, it is desirable to use a support which has significant porosity in the range between 30 and 100Å, e.g., > 0.01 cc/gm pore volume in the range of 30 and 100Å.

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Preferred Catalyst

The preferred catalyst comprises promoted copper bromide on a zirconia support. At the temperatures of operation contemplated in this process, the copper bromide does not substantially migrate from

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the catalyst composition nor among different regions of the catalyst and is very active. This high activity permits the use of comparatively lower temperatures thereby enhancing, even more, the catalyst's stability.

5 This preferred catalyst is produced by placing copper bromide directly onto the support, and is not made by converting another copper-bearing material into copper bromide on the support. Although we believe that the direct addition of the copper bromide to the support is
10 critical to the stability and activity of the catalyst, we do not wish to be bound to that theory. Additionally, the addition of certain promoters to the supported copper bromide catalyst appears to add substantial stability to the catalyst. Finally, although the support most
15 desirably comprises a zirconium-containing material such as zirconia, other supports are suitable.

Specifically the preferred catalyst is a composite comprising or desirably consisting essentially of copper bromide; promoter/stabilizer selected from
20 materials containing one or more salts, oxides, or complexes of metals selected from Ca, Y, Nd, or La or of metals having an ionic radius between about 0.9 and 1.4 Å; and an oxidic zirconium-containing catalyst support. The preferred promoters are Nd and La. Most preferred is
25 La.

The copper bromide should be present in at least a catalytic amount, that is to say, an amount sufficient at least to catalyze the reaction of HBr and oxygen to produce Br₂. We have found that copper bromide
30 in the amount of 0.1 % to 20 % (by weight) of the overall composition is desirable; 1.0 % to 6 % (by weight) of copper bromide is more desirable and 3.0 % to 6.0 % (by weight) of copper bromide is most desirable.

We have found that the introduction of the
35 copper catalyst onto the zirconium-containing catalyst

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support in the form of copper bromide results in a catalyst composition which is both more stable and more active than compositions in which the catalyst is introduced in another form, such as by the oxide. We have additionally found that the x-ray diffraction spectrum (Cu_α) of the catalyst composition does not show the presence of crystalline CuBr_2 . Specifically, the x-ray diffraction spectrum of crystalline CuBr_2 contains the following lines:

10

<u>2θ ($^\circ$)</u>	<u>I/I_0</u>
14.485	1.0
29.063	1.0
36.041	0.85

15

The absence of the most distinctive line ($2\theta = 14.485^\circ$) demonstrates the substantial absence of copper bromide crystallinity. Catalyst compositions prepared using CuO , which converts to copper bromide in the HBr oxidation process, show the presence of that distinctive line ($2\theta = 14.485^\circ$). We believe this to indicate that the copper bromide introduced to the zirconium-containing support, in contrast to copper bromide produced on the support from another material, is essentially amorphous.

25

We have not, however, found the source of the promoters/stabilizers to be of significant importance. Any salt or complex of the noted metals, whether oil or water soluble, which can be impregnated onto the zirconium-containing support or mixed with the zirconium support, e.g., as by ball milling with the zirconium support precursor, is suitable. The bromide salts are especially suitable, but other halides (iodide or chloride), oxyhalides, oxides, phosphates, sulfides, sulfates; complexes such as acetylacetonates, and the like are also suitable. Lanthanum bromide, oxybromide,

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oxide, and mixtures are useful and conveniently available. The promoter/stabilizer metal-bearing material should be present in an amount such that the overall content (in whatever form) is desirably between
5 0.1 % and 10 % (by weight) of the overall composition; 1.0 % to 6.0 % (by weight) is more desirable; 1.0 % to 4.0 % (by weight) is most desirable.

The zirconium-containing support typically should contain more than about 50% (wt) of zirconia. A
10 minor amount of other metal oxides, e.g., alumina, titania, yttria, hafnia, silica, etc., may be included as a binder or extrusion aid or to increase the surface area or porosity if so desired. We have found that it is very desirable to use a zirconia support which has significant
15 porosity in the range between 30 and 100Å, e.g., > 0.01 cc/gm pore volume in the range of 30 and 100Å.

General

The catalyst material may be utilized in any
20 physical form convenient to the process in which it is utilized. Such forms may include tablets, extrudates, raschig rings, Pall rings, or the like. The reaction is very exothermic and consequently the relative external surface area may be an important consideration in some
25 reactor/process configurations.

The catalyst desirably is prepared by dissolving the appropriate catalyst metal and the promoter/stabilizer metal compounds or complexes independently in aqueous acid, preferably HBr, solutions
30 and impregnating them into the catalyst supports. The catalyst supports should be dried at, e.g., 110° to 135°C in air, before impregnation so to allow accurate measurement of the metal content added to the support. The method and sequence of impregnating the support has
35 not been found to be critical. If the various compounds

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are compatible, e.g., they don't react together and don't precipitate from solution, a single solution containing the metals may be used as the impregnating solution. Depending upon the impregnating procedure chosen, the solutions may be saturated or not. If an incipient wetness method is selected, the amount of solution will match the pore volume of the support requiring that the composition of the solution be adjusted to assure that the amount of metal added to the support is appropriate. If other procedures are elected, saturated solutions may be used and a particular amount of the solutions chosen. The impregnated support is dried and ready for use.

The invention has been disclosed by direct description. Below may be found a number of examples showing various aspects of the invention. The examples are only examples of the invention and are not to be used to limit the scope of the invention in any way.

EXAMPLESExample 1

5 This example shows a long term test of the a highly desired $\text{CuBr}_2/\text{LaBr}_3/\text{ZrO}_2$ catalyst in the HBr oxidation step.

A pure zirconia support having a pore size distribution of 0.093 cc/gm of pore volume in the range of 30-100Å and 0.098 cc/gm in the range of 600-1000 Å
10 pore diameter was used to prepare the $\text{CuBr}_2/\text{LaBr}_3/\text{ZrO}_2$ catalyst. The support was a powdered zirconia support which was impregnated with solutions of CuBr_2 and LaBr_3 and pressed in a die using a carved press. This pressing was then ground and sieved to give a 20-30 mesh fraction.
15 The finished catalyst contained 0.2 mmoles/cc of CuBr_2 and 0.6 mmoles/cc of LaBr_3 . The pore size distributions were determined using a Micromeritics Autopore II 9220 mercury porosimeter.

The catalyst was tested for activity using the
20 following procedure:

A 1 cm OD by 45 cm long glass reactor tube was filled to about its length-wise center with glass beads. A glass wool plug was then inserted. About 1 cc of catalyst was placed on the glass wool. Another glass
25 wool plug was placed over the catalyst bed. The remainder of the glass tube was packed with glass beads. The glass reactor was then placed in a tube furnace with an aluminum sleeve between the outer reactor wall and the inner wall of the furnace to aid in heat distribution. A
30 thermocouple was included at the center of the catalyst bed. A 48% HBr solution was delivered to the reactor at a rate of 6 cc/hr using a syringe pump. During the test, the syringe pump had to be refilled about every 20 hours. During the refilling period, nitrogen flowed through the
35 reactor. Upon readmittance of HBr to the reactor, an

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initially lower reaction rate was observed in the first 20 minutes of testing. However, the rate then returned to the rate prior to the refilling of the syringe.

Oxygen was fed to the reactor using a mass flow controller at a rate of 6 cc/hr. The temperature of the reactor was maintained at 275°C.

The reaction products and unreacted feed materials were condensed in traps containing KI. In the traps, the product Br_2 formed reacts there with the KI to form the I_3^- ion. The I_3^- ion was then titrated with $\text{Na}_2\text{S}_2\text{O}_3$. The amount of bromine formed in the reactor was calculated from the titration results. The reactor effluent was collected in the traps, measured at various intervals, and the reaction rates calculated. The measured rate at intervals over the 100 hours is shown in the Table. The data show no decrease in activity over the 100 hour run, and perhaps show some increase in activity during that period. This indicates good long term life for the $\text{CuBr}_2/\text{LaBr}_3/\text{ZrO}_2$ catalyst.

Table	
Time on Stream (hrs)	Rate ($\mu\text{mol-cc}^{-1}\text{-sec}^{-1}$)
2	2.7
20	3.2
50	2.9
80	3.7
100	4.1

Example 2

This example shows the use of the preferred $\text{CuBr}_2/\text{LaBr}_3/\text{ZrO}_2$ oxidation catalyst in the temperature
5 range between 150°C and 350°C .

The catalyst was tested as in Example 1; again, the rate of 48% HBr feed was 6 cc/hr, and the rate of O_2 feed was 6 cc/min. The temperature was varied to produce bed temperatures ranging from 150° to about 350°C .
10 Figure 6 shows the average reaction rates for the catalyst as a function of temperature for a 2 hour test.

Example 3

This example shows the use of an homogeneous
15 catalyst system for conversion of HBr to Br_2 . A 250 ml Fisher-Porter bottle equipped with an overhead stirrer was charged with 30 g Cu_2Br_2 (as catalyst) and 110 ml of 48% HBr. The assembly was placed in an oil bath and brought to about 135°C . The stirring rate was 750 rpm.
20 Anhydrous HBr was metered to the reactor at 350 ml per minute and O_2 was fed at 750 ml per minute. The total pressure was maintained at 50 psig. A gas stream continuously stripped any Br_2 formed in the system, which Br_2 was trapped downstream using a KI trap. The trap
25 operated to detect the amount of Br_2 formed in the reactor by reacting with the Br_2 to form the I_3^- ion. The I_3^- ion was titrated with NaS_2O_3 and the amount of produced Br_2 was calculated using the result. The traps were checked about every ten minutes. Figure 7 shows the
30 rate of Br_2 production as a function of time. This example shows the effectiveness of the catalyst in oxidizing HBr to Br_2 .

This invention has been described using
examples to show preferred embodiments. It will be
35 apparent to those skilled in the art that modifications

and changes may be made which still fall within the spirit and scope of the attached claims.

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WE CLAIM AS OUR INVENTION:

1. A process for producing Br_2 from seawater comprising the steps of:

- a. acidifying the seawater with sulfuric acid,
- b. chlorinating the acidified seawater,
- c. aerating the acidified, chlorinated seawater to produce a bromine depleted seawater stream and a dilute $\text{H}_2\text{O}/\text{Br}_2$ stream,
- d. mixing the dilute $\text{H}_2\text{O}/\text{Br}_2$ stream with SO_2 to form an acid stream comprising HBr , H_2SO_4 , and air,
- e. separating the air from the remainder of the acid stream,
- f. separating the HBr from the H_2SO_4 and forming a HBr reactor feedstream,
- g. contacting the HBr reactor feedstream and an O_2 -containing gas with a catalyst composition to convert at least a portion of the HBr to Br_2 and produce a reaction effluent stream, and
- h. recovering the Br_2 product.

2. The process of claim 1 where the catalyst composition comprises an active catalyst selected from the metals, and oxides, halides, and oxyhalides of the following metals: Group IB, Group IVB, Group VB, Group VIB, Group VIIB, Group VIII, and the rare earth lanthanide series.

3. The process of claim 2 where the catalyst composition additionally comprises a promoter and a catalyst support selected from MgO , Al_2O_3 , ZrO_2 , HfO_2 , SiO_2 , bentonite, attapulgite, and pumice.

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4. The process of claim 2 where the catalyst composition is an homogeneous liquid.
5. The process of claim 3 where the catalyst composition comprises copper bromide, a promoter, and an oxidic zirconium-containing catalyst support.
6. The process of claim 5 where the copper bromide content of the catalyst composition is within the range of about 0.1 % to 20 % by weight.
7. The process of claim 6 where the overall copper bromide content of the catalyst composition is within the range of about 1 % to 10 % by weight.
8. The process of claim 7 where the overall copper bromide content of the catalyst composition is within the range of about 0.1 % to 6 % by weight.
9. The process of claim 5 in which the promoter is selected from compounds or complexes of Ca, Y, Nd, or La.
10. The process of claim 9 in which the promoter is a lanthanum-containing compound comprising lanthanum bromide, lanthanum oxybromides, or a mixtures thereof.
11. The process of claim 10 in which the promoter is present in an amount between 0.1 % and 10 % (by weight) of the catalyst composition.
12. The process of claim 5 in which the zirconium-containing catalyst support comprises zirconia.
13. The process of claim 10 in which the zirconium-containing catalyst support comprises zirconia.

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14. The process of claim 12 where the catalyst's x-ray diffraction graph shows substantially no peak at $2\theta = 14.485^\circ$.

5 15. The process of claim 11 in which the porosity of the zirconia is greater than about 0.01 cc/gm pore volume in the range of about 30-100 Å pore diameter.

10 16. The process of claim 5 in which the molar ratio of HBr:O₂ is between about 3.25 and 4.1.

17. The process of claim 16 in which the molar ratio of HBr:O₂ is between about 3.9 and 4.0.

15 18. The process of claim 1 in which the Br₂ product recovery is effected by quenching the reaction effluent in a quench stream containing HBr and removing unreacted HBr, absorbing Br₂ from the quenched reaction effluent in a stream containing aqueous NaBr to form a Br₂ absorbate stream and a water phase, desorbing Br₂ from the Br₂ absorbate stream, decanting Br₂ from the water phase to produce a Br₂ product stream.

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25 19. The process of claim 18 additionally comprising the step of drying the Br₂ product stream by contacting it with strong H₂SO₄.

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20. A process for producing Br_2 from seawater comprising the steps of:

- a. acidifying the seawater with sulfuric acid,
- 5 b. chlorinating the acidified seawater,
- c. aerating the acidified, chlorinated seawater to produce a bromine depleted seawater stream and a dilute $\text{H}_2\text{O}/\text{Br}_2$ stream,
- 10 d. mixing the dilute $\text{H}_2\text{O}/\text{Br}_2$ stream with SO_2 to form an acid stream comprising HBr , H_2SO_4 , and air,
- e. separating the air from the remainder of the acid stream,
- 15 f. separating the HBr from the H_2SO_4 and forming a HBr reactor feedstream,
- g. contacting the HBr reactor feedstream with an O_2 -containing gas in a molar ratio of $\text{HBr}:\text{O}_2$ between about 3.25 and 4.1 with a catalyst composition comprising copper bromide in an amount such that the overall copper bromide content of the composition is within the range of about 1 % to 10 % by weight, a lanthanum-containing compound selected from the group of lanthanum oxide, lanthanum bromide, lanthanum oxybromides, or mixtures thereof, and a zirconia catalyst support to convert at least a portion of the HBr to Br_2 and produce a reaction effluent stream, and
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- 5
- h. quenching the reaction effluent in a quench stream containing HBr and removing unreacted HBr,
 - i. absorbing Br_2 from the quenched reaction effluent in an aqueous stream containing NaBr to form a Br_2 absorbate stream,
 - j. desorbing Br_2 from the Br_2 absorbate stream, and
 - 10 k. decanting Br_2 from a water phase of produce a Br_2 product stream.

15 21. The process of claim 20 additionally comprising the step of drying the Br_2 product stream by contacting it with strong H_2SO_4 .

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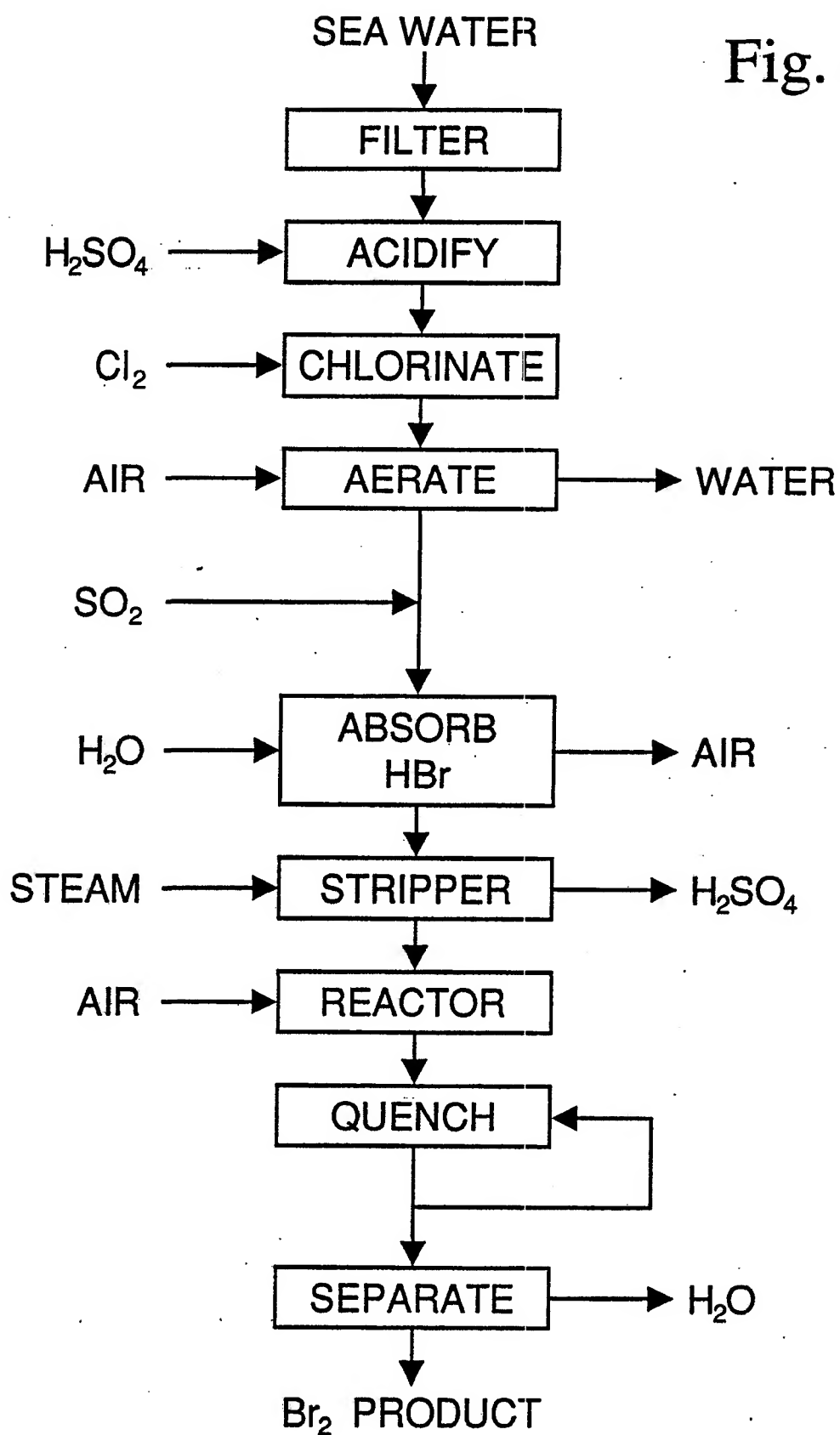
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Fig. 1



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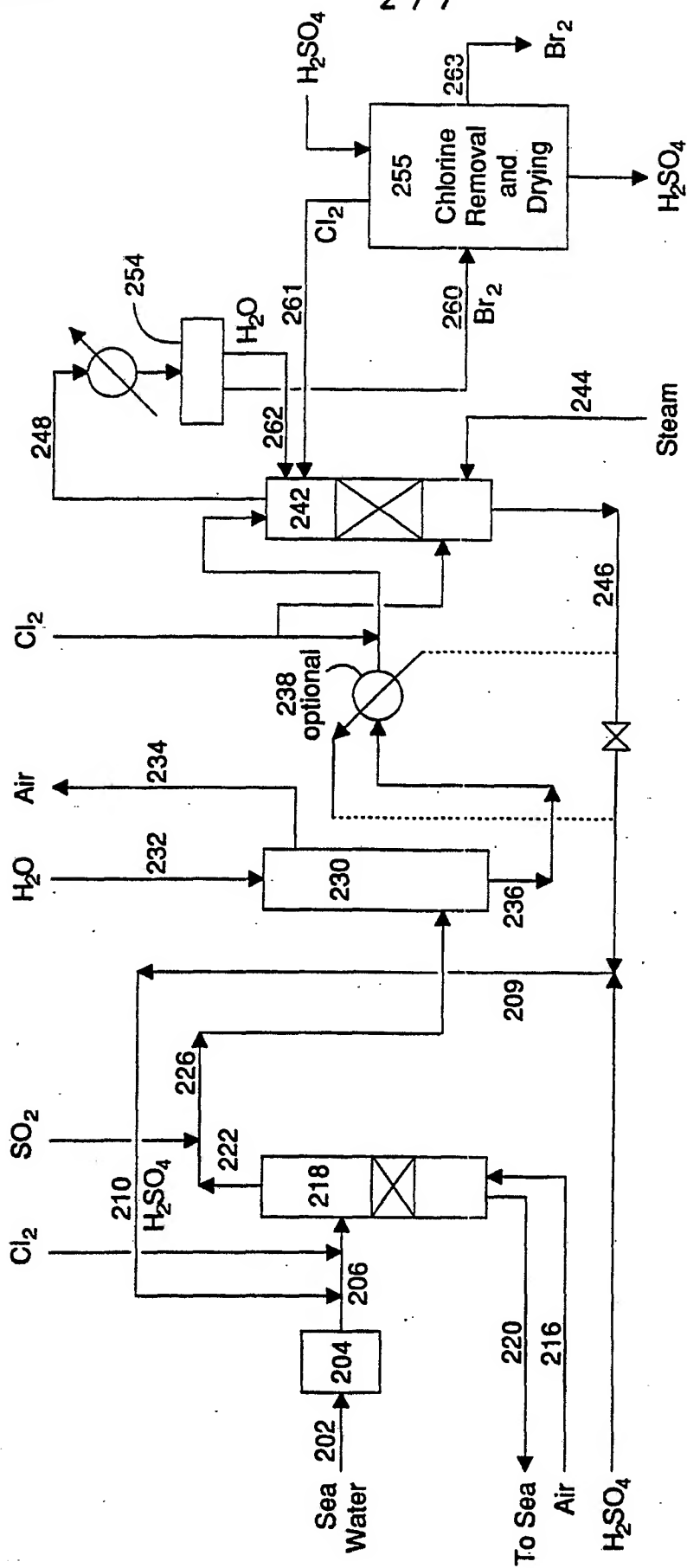


Fig. 2

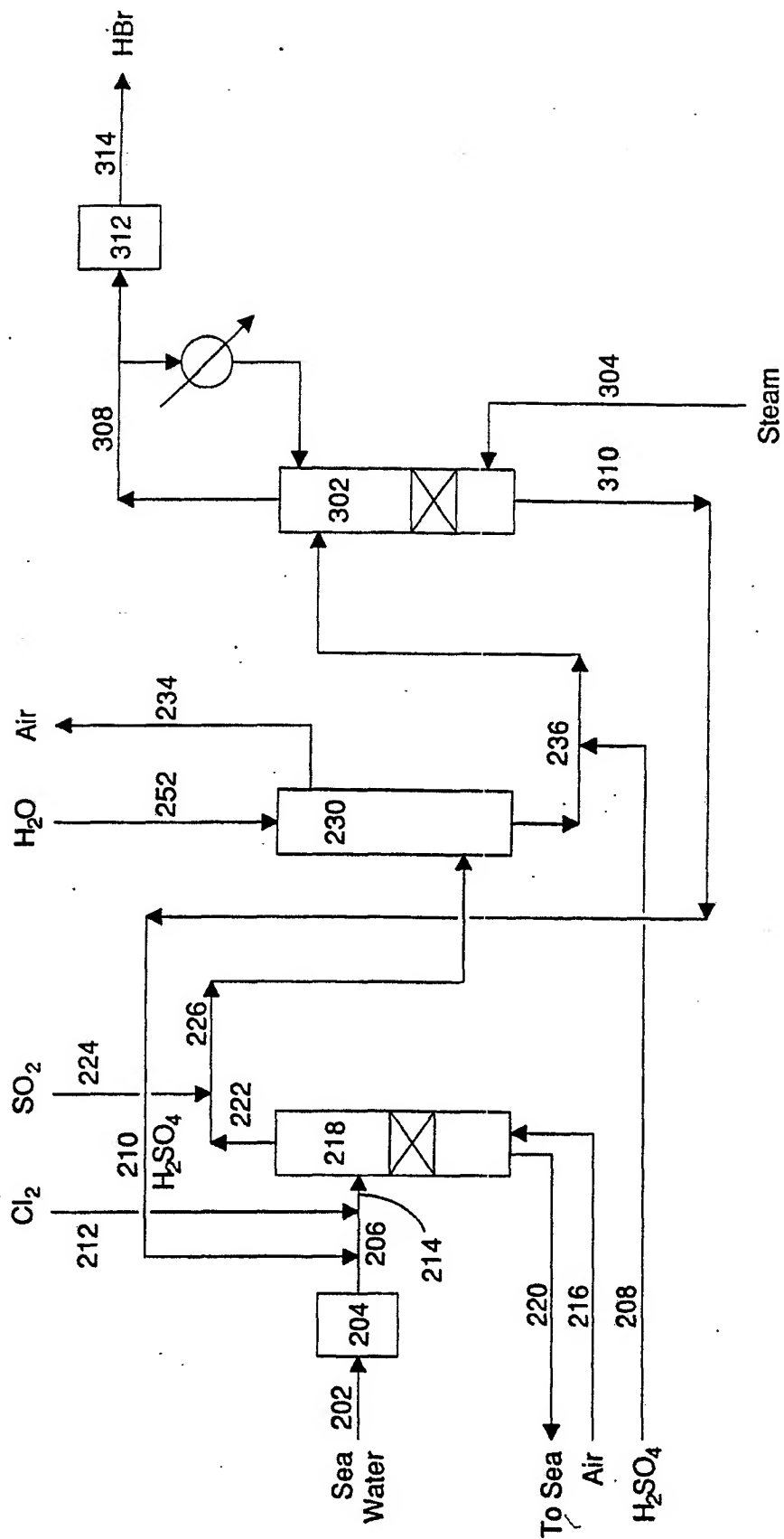
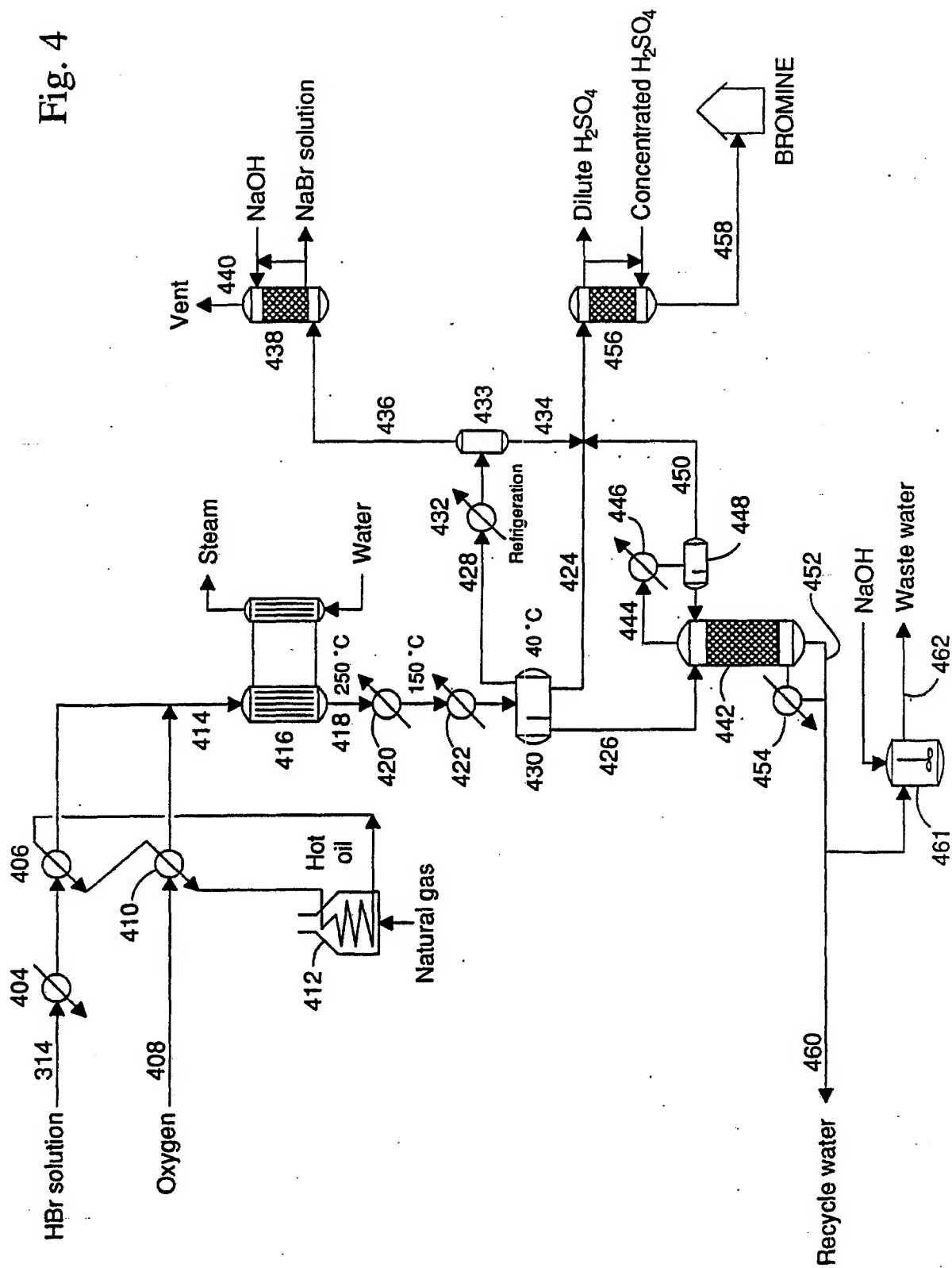


Fig. 3

Fig. 4



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Fig. 5

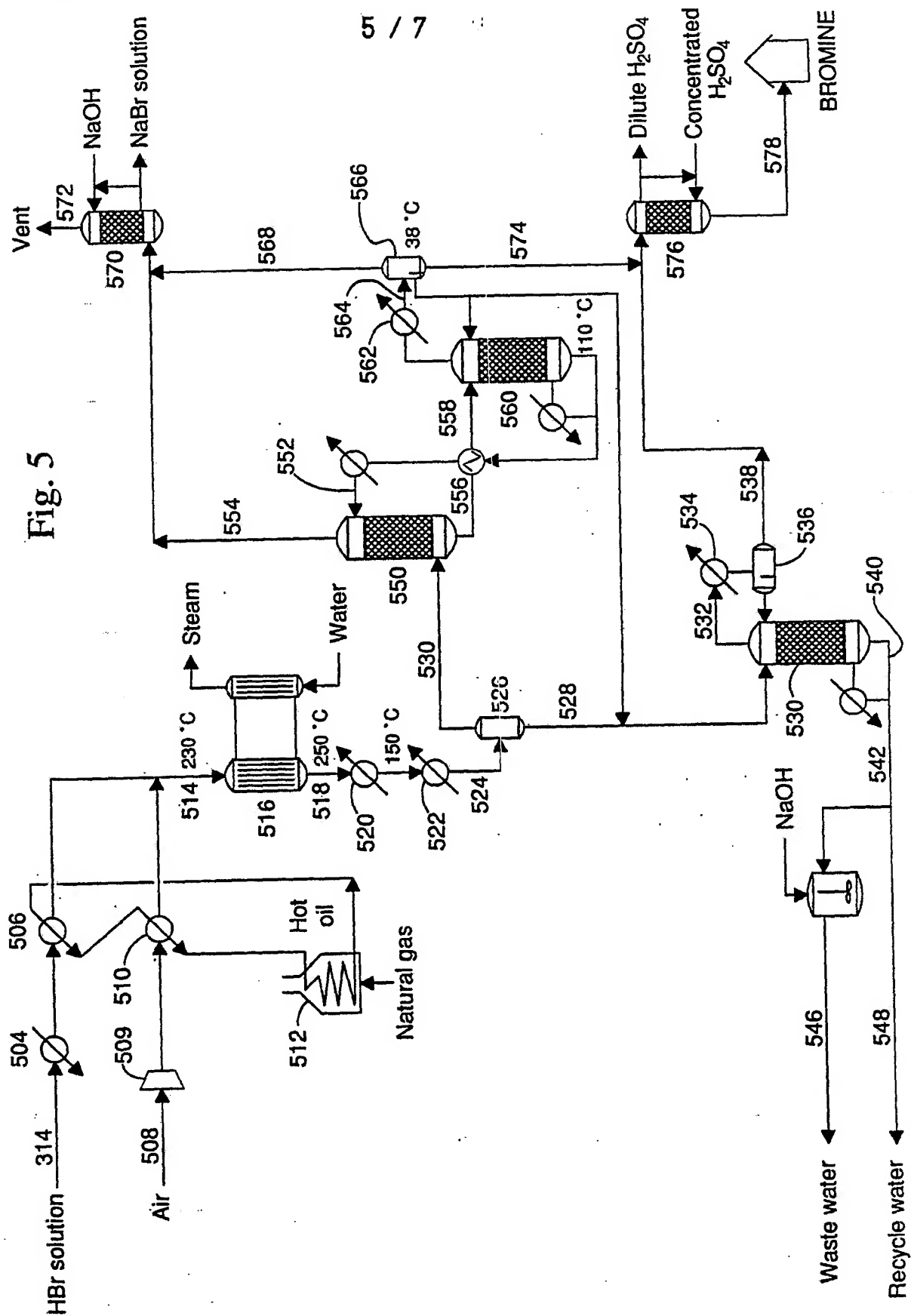


Fig. 6

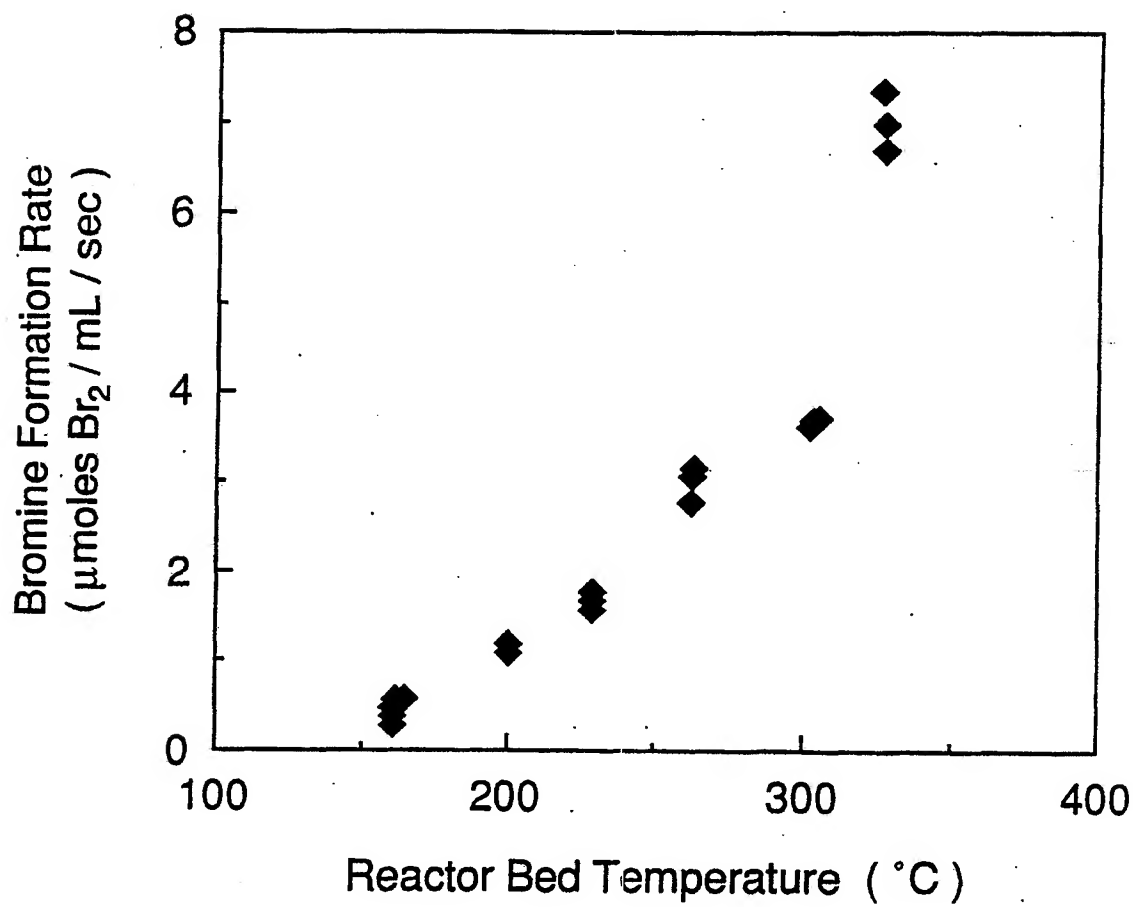
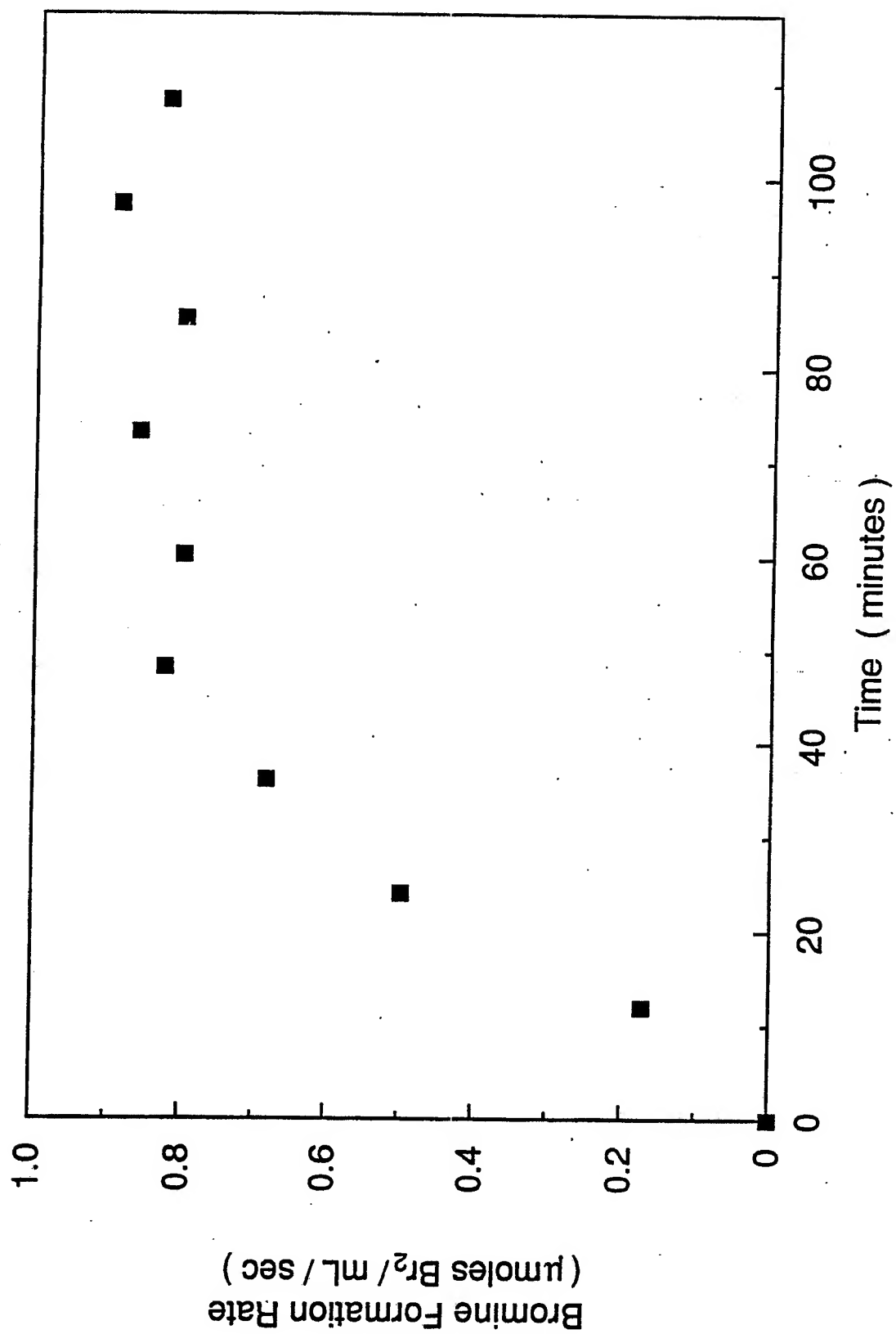


Fig. 7



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INTERNATIONAL SEARCH REPORT

PCT/US92/07822

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C01B 7/09

US CL :423/502

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/500,423/503,423/488,423/481

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 2,536,457 (Mugdan) 02 January 1951, See column 1, line 24; column 2, lines 10-25, 40-46; column 3, lines 25-26, column 4, lines 30-70, column 5, lines 1-10 and figure.	1-4,18,20
Y	US,A, 2,143,233 (Heath) 10 January 1939 1936, See figure and claim 2.	1-4,18,20
Y	JP,A, 38-20358 (Shell) 03 October 1963, See column 1 and column 2.	5-17,20
Y	CA,A, 615,926 (Deahl, et al.) 07 March 1961, See column 1, lines 20-25 and column 2, lines 28-32.	5-17,20

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance		
E earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed	*Z*	document member of the same patent family

Date of the actual completion of the international search 05 NOVEMBER 1992	Date of mailing of the international search report 14 JAN 1993
Name and mailing address of the ISA/ Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer VALERIE ANN LUND <i>Valerie Ann Lund</i>
Facsimile No. NOT APPLICABLE	Telephone No. (703) 308-1304

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/07822

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	BE,A,651,747 (Ratkuv) 12 February 1965, See abstract.	19 & 21
Y	US,A, 2,163,877 (Hooker) 27 June 1939 See column 3, lines 1-25 and column 2.	1,20
A	US,A, 3,816,599 (Kafes) 11 June 1974, See column 3, lines 1-40.	1-20
A	US,A, 4,119,705 (Riegel) 10 October 1978 See abstract and claim 1.	1,20
A	FR,A, 1,291,932 (California Research) 19 March 1962, See abstract and column 2.	1,20
A	Chemical Engineering Science, Vol. 23, 20 February 1968 Ruthven, et al., "The Kinetics of the Oxidation of Hydrogen Chloride Over Molten Salt Catalyst" pages 981-988.	1,20